Crystal structures of the α''-cerium phases

(metallic element/high pressure/metastable phases)

W. H. ZACHARIASEN

Department of Physics, University of Chicago, Chicago, Illinois 60637

ABSTRACT   Endo et al. [Endo, S., Sasaki, H. & Mitsui, T. (1972) J. Phys. Soc. Jpn. 42, 882–885] have reported x-ray diffraction data for an unidentified phase of cerium metal observed in the 50- to 100-kbar range. It is shown that the unknown phase is a variant of the metastable monoclinic phase, α''-Ce, previously observed. The complete structure of the new form of α''-Ce is deduced.

Two phases of cerium metal, α'-Ce and α''-Ce, have been shown to exist at room temperature in the pressure range 51–100 kbar (1–3). α'-Ce is orthorhombic and has the α uranium type of structure. α''-Ce is monoclinic body-centered with two atoms per unit cell and has a distorted cubic face-centered structure. Pressure cycling induces the transition α''-Ce $\rightarrow$ α'-Ce, showing that α''-Ce is the metastable form and α'-Ce the stable form. The atomic volume, V_A, of α'-Ce and of α''-Ce is the same within experimental error at the same pressure. However, at the transformation pressure of 51 kbar, the α-Ce $\rightarrow$ α'-Ce transition is accompanied by a volume decrease of $\Delta V/V = -0.012 \pm 0.002$.

Recently, Endo et al. (4) described results of "in situ" x-ray diffraction studies of cerium metal (at room temperature) up to pressures of 175 kbar. They reported the presence of an unidentified phase in the 50- to 100-kbar range and gave the observed intensities and spacings, d, for 17 diffraction lines of this phase at a pressure of 67 kbar. These diffraction data are shown in the first three columns of Table 1.

Interpretation of the diffraction data of Table 1

Thirteen of the diffraction lines of Table 1 can be attributed to the monoclinic body-centered α''-Ce phase with two metal atoms per unit cell. The cell dimensions obtained by analysis of the data are shown in Table 2 with the cell constants reported by Zachariasen and Ellinger (2) for α''-Ce at 56 kbar and 100 kbar, as deduced from the diffraction data of Schaufelberger and Merx (5). If one assumes the pressures reported in ref. 5 to be correct, the atomic volume suggests that the pressure of 67 kbar given by Endo et al. is too high by about 6 kbar.

Lines 1, 9, 15, and 17 of Table 1 are not accounted for. However, they can be explained as "superstructure" lines of α''-Ce, requiring a doubling of the cell volume.

Let the form of α''-Ce corresponding to the cell dimension of Table 2 be designated α''-Ce(I) and the form of α''-Ce corresponding to the diffraction pattern of Table 1 be designated α''-Ce(II). If a', b', c' be the vector axes of the body-centered cell of Table 2, the axes a, b, and c of the larger cell of α''-Ce(II) are defined by the relationships: $a = -a' + c'$, $b = b'$, and $c = a' + c'$. The dimensions of the unit cell of α''-Ce(II) accordingly become: $a = 5.813(6)$ Å, $b = 3.148(5)$ Å, $c = 5.622(5)$ Å, and $\beta = 112.85(10)°$. The Miller indices of the diffraction lines according to the smaller ($H'K'L'$) and the larger (HKL) cell are shown in Table 1.

The unit cell of α''-Ce(II) is base-centered, and the space group is $C2/m$ with the four cerium atoms in positions $\pm(x, 0, z)$ ($\frac{1}{2} + x$, $\frac{1}{2}$, z). If $x = z = \frac{1}{4}$, the structure becomes face-centered and can be described in terms of the smaller, body-centered unit cell of α''-Ce(I). Because the "superstructure" lines are weak or absent, it follows that $x \approx \frac{1}{4}$, $z \approx \frac{1}{4}$. Indeed, the observed intensities indicate $x = 0.278 \pm 0.008$, $z = 0.250 \pm 0.008$.

In the α''-Ce(II) structure, each cerium atom has 12 neighbors, 1 at 2.99 Å, 2 at 3.13 Å, 2 at 3.15 Å, 4 at 3.31 Å, 2 at 3.35 Å and 1 at 3.36 Å. A shift of the atoms by only 0.16 Å would transform the α''-Ce(II) structure into the α''-Ce(I) structure in which a cerium atom has two neighbors at 3.15 Å, two at 3.16 Å, four at 3.22 Å, and four at 3.31 Å. Were $x = z = \frac{1}{4}$, $\beta = \cos^{-1}(-\frac{1}{3}) = 109.47°$, and $a:b:c = 3^{1/2}:1:3^{1/2}$, the structure would become cubic face-centered; and were the atomic volume unchanged, each cerium atom would have 12 neighbors at 3.226 Å. Thus, the distortion from a cubic face-centered structure is only a little greater for α''-Ce(II) than it is for α''-Ce(I).

Table 1.   Interpretation of diffraction data of table 2 of ref. 4

Line	d_{obs}, Å	Intensity*	$H'K'L'$	HKL	d_{calc}, Å
1	2.889	m		$20\bar{1}$	2.880
2	2.679	vs	$10\bar{1}$	200	2.680
3	2.628	vs	110	$11\bar{1}$	2.625
4	2.591	w	101	002	2.593
5	2.381	s	200	$20\bar{2}$	2.382
6	2.238	m	011	111	2.232
7	1.650	m	$21\bar{1}$	$31\bar{1}$	1.649
8	1.589	w	002	$31\bar{2}$	1.590
				202	1.582
9	1.553	t		310	1.554
10	1.439	m	$30\bar{1}$	$40\bar{2}$	1.440
				$40\bar{1}$	1.439
11	1.421	w	310	$31\bar{3}$	1.417
12	1.340	w	$20\bar{2}$	$40\bar{3}$	1.340
				400	1.340
13	1.313	w	220	$22\bar{2}$	1.313
14	1.188	t	400	$40\bar{4}$	1.191
				401	1.190
				$22\bar{3}$	1.187
15	1.090	vw		$51\bar{2}$	1.091
16	1.065	vw	$32\bar{1}$	$42\bar{2}$	1.063
				$42\bar{1}$	1.063
			$41\bar{1}$	$51\bar{3}$	1.062
17	1.017	t		510	1.015

* Intensity: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; t, trace.

Physics: Zachariasen

Proc. Natl. Acad. Sci. USA 75 (1978) 1067

Table 2. Dimensions of smaller monoclinic cell

	This paper	Ref. 2	Ref. 2
P, kbar	67	56	100
a', Å	4.764(5)	4.762(6)	4.686(6)
b', Å	3.148(5)	3.170(5)	3.073(5)
c', Å	3.163(5)	3.169(5)	3.089(5)
β', deg	92.08(10)	91.73(15)	92.69(15)
V_A, Å^3	23.70	23.91	22.22

Numbers in parentheses give uncertainty of last decimal place.

Calculated and observed intensities

The spacings of the diffraction lines of Table 1 are satisfactorily explained by the unit cell with four atoms given above for α''-Ce(II). However, it needs to be demonstrated that the observed intensity estimates are in accord with the proposed structure. It is convenient to use the simplified intensity expression $I_{calc} = Cp|F|^2d^2$, in which C is a scale factor, p is the multiplicity, F is the structure factor, and d is the spacing.

The measurements of Endo *et al.* (4) were made in the plane normal to the axis of their x-ray camera, and the intensity of only a very small arc of the Debye–Scherrer circle was recorded on the film. Thus, their diffraction patterns give no direct evidence of the presence of preferred orientation effects. However, such effects are normally present in diffraction patterns taken at high pressure and require large intensity corrections.

The observations indicate that the axis of the preferred orientation normal to the plane of observation is the reciprocal axis c^* and that the b axis tends to line up parallel to the incident beam. Let γ_1, γ_2, and γ_3 be the direction cosines of the normal to the reflecting plane (HKL) in the cartesian system defined by the vectors a, b, and c^*. One finds readily:

$$\gamma_1 = Hd_{HKL}/a, \quad \gamma_2 = Kd_{HKL}/b, \quad \gamma_3$$
$$= (-Ha^* \cos \beta + Lc^*) d_{HKL}.$$

An approximate measure of the effect of preferred orientation on intensity measurement made in the equatorial plane is the quantity exp $(-\alpha k)$, in which α is an adjustable constant (chosen to be 2.2) and $k = \gamma_2^2 + \gamma_3^2 = 1 - \gamma_1^2$. Thus, the observed intensity estimates should be compared with the corrected calculated intensities $I_{corr} = I_{calc}$ exp $(-2.2k)$.

Table 3 lists the complete set of possible reflections of α''-Ce(II) up to scattering angle $2\theta = 30°$, the calculated and observed spacings, the intensities I_{calc} and I_{corr}, and the observed intensity estimates. It is seen that the calculated intensities corrected for preferred orientation effects are in good agreement with the reported intensity estimates.

Discussion

It is not known at the present time why the transformation at about 51 kbar sometimes leads to the formation of the stable phase α'-Ce and at other times to the formation of the meta-

Table 3. Observed and calculated intensities

HKL	d_{calc}, Å	d_{obs}, Å	I_{calc}	I_{corr}	I_{obs}*
001	5.181		0	0	
20$\bar{1}$	2.880	2.889	0.8	2.1	m
110	2.715		0	0	
200	2.680	2.679	4.8	10.0	vs
11$\bar{1}$	2.625	2.628	10.0	5.0	vs
002	2.593	2.591	5.0	1.6	w
20$\bar{2}$	2.382	2.381	3.6	5.0	s
111	2.232	2.238	6.6	2.3	m
11$\bar{2}$	2.092		0.2	0.1	
201	2.075		0.3	0.3	
20$\bar{3}$	1.807		0.2	0.2	
003	1.729		0	0	
112	1.714		0.1	0	
31$\bar{1}$	1.649	1.650	2.2	3.5	m
11$\bar{3}$	1.608 ⎫		2.7 ⎫	1.0 ⎫	
31$\bar{2}$	1.590 ⎬	1.589	0.7 ⎬	0.9 ⎬	w
202	1.582 ⎭		1.2 ⎭	0.7 ⎭	
020	1.574		1.3	0.4	
310	1.554	1.553	0.6	0.8	t
021	1.506		0	0	
40$\bar{2}$	1.440 ⎫		0.6 ⎫	1.6 ⎫	m
40$\bar{1}$	1.439 ⎭		0.4 ⎭	1.2 ⎭	
31$\bar{3}$	1.417	1.421	1.4	1.5	w
20$\bar{4}$	1.399		0.8	0.4	
22$\bar{1}$	1.381		0.2	0.1	

* As in Table 1.

stable phases α''-Ce(I) or α''-Ce(II), or to the formation of a mixture of α'-Ce and α''-Ce phases. Small impurities, rate of change of pressure, thermal and pressure history of the sample, and anisotropy of the applied pressure are possible factors that could influence the nature of the transition.

Endo *et al.* (4) report the discovery of still another high-pressure form of cerium metal, stable above 121 kbar. The new phase is tetragonal body-centered with two atoms per unit cell. The atomic volume is reported to be 21.8 Å^3 at 121 kbar and 20.6 Å^3 at 175 kbar.

One would expect that the transition from α'-Ce (or α''-Ce) to the new tetragonal phase would be accompanied by a very small volume decrease. The atomic volume data for α'-Ce of ref. 3 for the range 41–95 kbar extrapolated to higher pressures suggest that the pressures reported in ref. 4, are too high. The extrapolation gives 112 kbar instead of 121 kbar and 146 kbar instead of the reported value of 175 kbar.

1. Ellinger, F. H. & Zachariasen, W. H. (1974) *Phys. Rev. Lett.* **32**, 773–774.
2. Zachariasen, W. H. & Ellinger, F. H. (1977) *Acta Crystallogr. Sect. A* **33**, 155–160.
3. Zachariasen, W. H. (1977) *J. Appl. Phys.* **48**, 1391–1394.
4. Endo, S., Sasaki, H. & Mitsui, T. (1977) *J. Phys. Soc. Jpn.* **42**, 882–885.
5. Schaufelberger, P. L. & Merx, H. (1975) *High Temp. High Pressures* **7**, 55–63.